

# STABILITY OF ATOMS AND MOLECULES IN AN ULTRARELATIVISTIC THOMAS–FERMI–WEIZSÄCKER MODEL

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ABSTRACT. We consider the zero mass limit of a relativistic Thomas–Fermi–Weizsäcker model of atoms and molecules. We find bounds for the critical nuclear charges that insure stability.

## 1. INTRODUCTION

The zero mass limit of the relativistic Thomas–Fermi–Weizsäcker (henceforth ultrarelativistic TFW) energy functional for nuclei of charges  $z_i > 0$  (which need not be integral) located at  $R_i$ ,  $i = 1, \dots, K$  is defined by [3, 4]

$$(1) \quad \xi(\rho) = a^2 \int (\nabla \rho^{1/3})^2 dx + b^2 \int \rho^{4/3} dx - \int V(x) \rho(x) dx + D(\rho, \rho),$$

Here  $\rho(x) \geq 0$  is the electron density,

$$(2) \quad V(x) = \alpha \sum_{i=1}^K \frac{z_i}{|x - R_i|},$$

the electrostatic potential created by the nuclei,

$$(3) \quad D(\rho, \rho) = \frac{\alpha}{2} \int \frac{\rho(x)\rho(y)}{|x - y|} dx dy,$$

the electronic repulsion, and  $\alpha = e^2/\hbar c \approx 1/137$  is the fine structure constant. In units in which  $\hbar = c = 1$ , the constants  $a^2$ , and  $b^2$  in (1) are given respectively by

$$(4) \quad a^2 = \frac{3}{8\pi^2} (3\pi^2)^{2/3} \lambda$$

and

$$(5) \quad b^2 = \frac{3}{4} (3\pi^2)^{1/3}.$$

In the non relativistic case, some emphasis has been placed on the question of an appropriate choice of the coefficient  $\lambda$  of the gradient term connected to the kinetic energy. The non relativistic gradient correction  $\lambda(\nabla \rho)^2/\rho$  was initially derived by Weizsäcker [14] with a value  $\lambda = 1$ , whereas the systematic gradient expansion by Kirznits [7, 6] leads to  $\lambda = 1/9$ . In the derivation of Tomishima and Yonei [13],  $\lambda = 1/5$ . Lieb [8, 9] showed, that the Weizsäcker term introduces a  $z^2$  correction

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to the leading  $z^{7/3}$  term of the non-relativistic ground state energy. Adapting the coefficient in front of the Weizsäcker term such that the correction agrees with the leading  $z^2$  correction of the non-relativistic quantum mechanics, the Scott correction, lead Lieb to propose  $\lambda = 0.185$ . In relativistic quantum mechanics, the leading energy correction remains unchanged whereas the Scott correction is smaller than in relativistic quantum mechanics [5], i.e., we cannot expect to have  $\lambda$  the same value as in the TFW functional. However, we are not yet in a position to proceed with Lieb's strategy and to infer the coefficient of the gradient correction from this. In particular that would require showing that the massive equivalent of the function  $\xi$  leaves indeed the leading energy contribution unchanged and the gradient term yields again a  $z^2$  correction.

Let us first consider the atomic case, i.e., the case  $K = 1$ ,  $z_1 = z$ ,  $R_1 = 0$ . Because of simple scaling considerations, if we minimize the energy functional (1) over all functions  $\rho$  for which each of the terms in (1) makes sense, the infimum of the energy functional is either zero or minus infinity. In the first case we say the atom is *stable*. Otherwise we say the atom is *unstable*. Our purpose here is to determine the range of values of the  $z_i$ 's for which the atom or molecule is *stable*. The following result holds in the atomic case (i.e., for  $K = 1$ ,  $z_1 = z$ ,  $R_1 = 0$ ) [1].

**Theorem 1.1.** *Let*

$$(6) \quad \xi(\rho) = a^2 \int (\nabla \rho^{1/3})^2 dx + b^2 \int \rho^{4/3} dx - \int z \alpha \frac{\rho}{|x|} dx + D(\rho, \rho),$$

with  $D(\rho, \rho)$  given by (3). Then

$$(7) \quad \inf \xi(\rho) = \begin{cases} -\infty & \text{for } z > \frac{4ab}{3\alpha} + \frac{7\pi a^3}{6b^3} \\ 0 & \text{for } z < \frac{4ab}{3\alpha} \end{cases}$$

where the infimum is taken over all nonnegative functions  $\rho(x)$ , such that  $\rho \in L^{4/3}(\mathbb{R}^3)$ ,  $\nabla \rho^{1/3} \in L^2(\mathbb{R}^3)$ , and  $D(\rho, \rho) < \infty$ .

*Remarks*

- i) It follows from (7) that if  $z < 4ab/(3\alpha)$  the atom is stable, whereas if  $z > 4ab/(3\alpha) + 7\pi a^3/(6b^3)$  the atom is unstable. The exact critical value of  $z$  ( $z_c$  say) dividing the region of stability from the region of instability is not known. However, it turns out that for the physical values of the constants the gap between the upper and lower bounds on  $z_c$  is less than one, and therefore negligible (see the following remarks).
- ii) For the physical values of  $a$  and  $b$  given by (4) and (5), the atom will be stable if  $z < \sqrt{3\lambda/2}/\alpha \approx 167.8\sqrt{\lambda}$ . Thus, if  $\lambda = 1/9$  (i.e., the value used by Kirznits, [7, 6]) the atom is stable if  $z < 56$ . If  $\lambda = 1/5$  (i.e., the value used by Tomishima and Yonei, [13]) the atom is stable if  $z < 75$ . Finally, using the value of Lieb [8, 9], the atom is stable if  $z < 73$ .
- iii) As for the value of the gap, using the physical values of the constants, one gets  $7\pi a^3/(3b^6) = (7/12\pi)\sqrt{3\lambda^3/2} < 0.021 < 1$  for all the values of  $\lambda$  considered above. Thus, the gap is negligible from the physical point of view.

For the molecular case, i.e., when  $K > 1$ , and  $V$  is given by (2) the following result was proven in [1].

**Theorem 1.2.** *Let*

$$(8) \quad \xi(\rho) = a^2 \int (\nabla \rho^{1/3})^2 dx + b^2 \int \rho^{4/3} dx - \int V \rho dx + D(\rho, \rho),$$

*with  $V$  given by (2) and  $D(\rho, \rho)$  given by (3). Then*

$$(9) \quad \inf \xi(\rho) = 0 \quad \text{if } Z = \sum_{i=1}^K z_i \leq \frac{4ab}{3\alpha},$$

*where the infimum is taken over all nonnegative functions  $\rho(x)$ , such that  $\rho \in L^{4/3}(\mathbb{R}^3)$ ,  $\nabla \rho^{1/3} \in L^2(\mathbb{R}^3)$ , and  $D(\rho, \rho) < \infty$ .*

The above result is just a trivial extension of the atomic to the molecular case, and in some sense is the best possible when the interaction between the nuclei is not taken into account. In fact, if we neglect the nuclear interaction one can always think of the possibility of putting all the nuclear charges at the same point and reducing the molecular case to the atomic case, which explains the condition (9) on  $Z \equiv \sum_{i=1}^K z_i$ . The deficiencies of the above result are obvious. The goal of this paper is to have a result that yields stability for reasonable values of the nuclear charges. For that purpose the nucleus–nucleus interaction

$$(10) \quad U \equiv \alpha \sum_{1 \leq i < j \leq K} \frac{z_i z_j}{|R_i - R_j|},$$

plays a key role, because it prevents the possibility of putting the nuclear charges on top of each other.

Our main result is the following theorem for the molecular case.

**Theorem 1.3.** *Let  $\xi(\rho)$  be given by (8) for functions  $\rho$  as in Theorem 1.2, with  $V$  given by (2). Then, we have stability, i.e.,*

$$\inf \xi(\rho) + U \geq 0$$

*provided*

$$(11) \quad 0 \leq z_i \leq \frac{4a}{3\alpha} b \sqrt{1-x}$$

*where  $x \in (0, 1)$  is the root of*

$$(12) \quad \frac{1-x}{x^3} = \frac{b^4}{a^2} \left(\frac{4}{3}\right)^2 \frac{1}{2\pi\alpha(4+9\alpha^4)}.$$

*Remark* For the physical values of  $a$  and  $b$  given by (4) and (5), and taken the physical value of the fine structure constant (i.e.,  $\alpha = 1/137$ ) in (12), Theorem 1.3 says that the molecule will be stable if each  $z_i \leq 55$ , if  $\lambda = 1/9$  (i.e., the value used by Kirznits, [7, 6]). If  $\lambda = 1/5$  (i.e., the value used by Tomishima and Yonei, [13]) the molecule is stable if each  $z_i \leq 74$ . Finally, using the value of Lieb [8, 9], the molecule is stable if each  $z_i \leq 71$ . These bounds on each individual nuclear charge are almost the same as those embodied in the atomic case (i.e., the ones given in Theorem 1.1 above).

In the next section we give the proof of Theorem 1.3.

## 2. IMPROVED RESULTS ON THE STABILITY OF MOLECULES

In this section we prove Theorem 1.3. Our proof relies in a *modified uncertainty principle* (see Theorem 2.1 below) which is of independent interest. As we mentioned in the introduction, the nucleus–nucleus interaction plays a key role in the stability of molecules. As in [2] we may use the fact that the energy is separately concave in the nuclear charges and each charge  $z_i$  varies between 0 and  $z$ . The minimum of a concave function is always on the boundary and hence the value of  $z_i$  wants to be either 0 or  $z$ . If it is zero we have one nucleus less and if it is  $z$  then we are in the case we are considering.

First we need some notation. We introduce the nearest neighbor, or Voronoi, cells [15]  $\{\Gamma_j\}_{j=1}^K$  defined by

$$(13) \quad \Gamma_j = \{x \mid |x - R_j| \leq |x - R_k|\}.$$

The boundary of  $\Gamma_j$ ,  $\partial\Gamma_j$ , consists of a finite number of planes. We also define the distance

$$(14) \quad D_j = \text{dist}(R_j, \partial\Gamma_j) = \frac{1}{2} \min\{|R_k - R_j| \mid j \neq k\}.$$

One of the key ingredients we need in the sequel is an electrostatic inequality of Lieb and Yau [11, 12]. Define a function  $\Phi$  on  $\mathbb{R}^3$  with the aid of the Voronoi cells mentioned above. In the cell  $\Gamma_j$ ,  $\Phi$  equals the electrostatic potential generated by all the nuclei except for the nucleus situated in  $\Gamma_j$  itself, i.e., for  $x \in \Gamma_j$ ,

$$(15) \quad \Phi(x) \equiv z \sum_{\substack{i=1 \\ i \neq j}}^K |x - R_i|^{-1}.$$

If  $\nu$  is any bounded Borel measure on  $\mathbb{R}^3$  (not necessarily positive) then

$$(16) \quad \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} |x - y|^{-1} d\nu(x) d\nu(y) - \int_{\mathbb{R}^3} \Phi(x) d\nu(x) + U \geq \frac{1}{8} z^2 \sum_{j=1}^K D_j^{-1}.$$

We will also need a *localization* result for the kinetic energy which will allow us to control the Coulomb potential near each nuclei. This localization result for the UTFW model is given by Theorem 2.1 below.

**Theorem 2.1** (Modified uncertainty principle). *For any smooth function  $f$  on the closed ball  $B_R$  of radius  $R$  we have the estimate*

$$a^2 \int_{B_R} |\nabla f(x)|^2 dx + b^2 \int_{B_R} f(x)^4 dx \geq ab \int_{B_R} \left[ \frac{4}{3|x|} - \frac{2}{R} \right] f(x)^3 dx.$$

*Remark* Notice that the factor  $4/3$  is best possible and it agrees with the sharp value given in Theorem 1.1.

To prove this theorem, we need the following preliminary result.

**Lemma 2.1.** *Let  $u(r)$  be any smooth function with  $u(R) = 0$ . Then the following uncertainty principle holds*

$$\left| \int_{B_R} (3u(|x|) + u'(|x|)|x|) f(x)^3 dx \right| \leq 3 \left( \int_{B_R} |\nabla f(x)|^2 dx \right)^{1/2} \left( \int_{B_R} u(|x|)^2 |x|^2 f(x)^4 dx \right)^{1/2}.$$

There is equality if and only if

$$f = \frac{1}{\lambda \int_0^r [su(s)] ds + C}$$

for some constants  $C$  and  $\lambda$ .

*Proof.* Set

$$g_i(x) = u(|x|)x_i$$

where  $u$  is a smooth function with  $u(R) = 0$  and note that

$$\begin{aligned} \int_{B_R} (3u(|x|) + u'(|x|)|x|)f(x)^3 dx &= \sum_j \int_{B_R} f(x) [\partial_j g_j(x)] f(x)^2 dx \\ &= \sum_j \int_{B_R} f(x) \partial_j (g_j f^2)(x) dx - 2 \sum_j \int_{B_R} f(x)^2 g_j(x) \partial_j f(x) dx. \end{aligned}$$

Integrating the first term by parts yields

$$\sum_j \int_{B_R} f(x) \partial_j (g_j f^2)(x) dx = - \sum_j \int_{B_R} \partial_j f(x) g_j(x) f(x)^2 dx + \int_{\partial B_R} f(x)^3 u(|x|) |x| dS(x),$$

where the boundary term vanishes since  $u(R) = 0$ . Thus,

$$\int_{B_R} (3u(|x|) + u'(|x|)|x|)f(x)^3 dx = -3 \sum_j \int_{B_R} f(x)^2 g_j(x) \partial_j f(x) dx.$$

Using Schwarz' inequality on the last term yields

$$\left| \int_{B_R} (3u(|x|) + u'(|x|)|x|)f(x)^3 dx \right| \leq 3 \left( \int_{B_R} |\nabla f(x)|^2 dx \right)^{1/2} \left( \int_{B_R} u(|x|)^2 |x|^2 f(x)^4 dx \right)^{1/2}.$$

Schwarz's inequality is an equality if and only if

$$\partial_j f = -\lambda g_j(x) f(x)^2,$$

which can easily be integrated and yields the stated function.  $\square$

*Proof of Theorem 2.1.* To prove the theorem, pick

$$u(r) = \frac{1}{2} \left( \frac{1}{r} - \frac{1}{R} \right)$$

in the lemma which leads to the inequality

$$\int_{B_R} \left[ \frac{1}{|x|} - \frac{3}{2R} \right] f(x)^3 dx \leq \frac{3}{2} \left( \int_{B_R} |\nabla f(x)|^2 dx \right)^{1/2} \left( \int_{B_R} \left( 1 - \frac{|x|}{R} \right)^2 f(x)^4 dx \right)^{1/2}$$

Next, applying the inequality between the arithmetic and geometric mean yields

$$a^2 \int_{B_R} |\nabla f(x)|^2 dx + b^2 \int_{B_R} \left( 1 - \frac{|x|}{R} \right)^2 f(x)^4 dx \geq ab \int_{B_R} \left[ \frac{4}{3|x|} - \frac{2}{R} \right] f(x)^3 dx,$$

from which the theorem follows.  $\square$

In order to prove our main result, we consider the total energy,  $\xi(\rho) + U$ , and we split the  $\int \rho^{4/3}$  term in two parts, i.e.,  $(b_1^2 + b_2^2) \int \rho^{4/3}$ . For later discussions, it is important to remark that the parameter  $b_2$  can be chosen arbitrarily in the interval  $(0, b)$ . Then we use Theorem 2.1 with  $f^3 = \rho$  and  $B_R = B_j$ , the largest ball inscribed in the corresponding Voronoi cell  $\Gamma_j$ , to get

$$(17) \quad \begin{aligned} \xi(\rho) + U \geq & b_1^2 \int_{\mathbb{R}^3} \rho^{4/3} dx - \int_{\mathbb{R}^3} V(x) \rho(x) \\ & + ab_2 \sum_{j=1}^K \int_{B_j} \left( \frac{4}{3|x-R_j|} - \frac{2}{D_j} \right) \rho(x) dx + D(\rho, \rho) + U. \end{aligned}$$

In order to cancel the Coulomb singularity inside  $B_j$  we choose the parameter

$$(18) \quad b_2 = \frac{3}{4} \frac{\alpha z}{a}.$$

The restrictions on  $b_2$  will give restrictions on  $z$  to insure stability.

With the help of the Voronoi cells we now define,

$$(19) \quad W(x) \equiv \Phi(x) + \frac{z}{|x - R_j|}$$

if  $x \in \Gamma_j$  and  $|x - R_j| \geq D_j$ , whereas,

$$(20) \quad W(x) \equiv \Phi(x) + \frac{2ab_2}{D_j},$$

if  $x \in \Gamma_j$  and  $|x - R_j| \leq D_j$ . Now, if we restrict to values of  $z$  such that  $z \leq 4ab_2/(3\alpha)$ , we can finally write

$$(21) \quad \xi(\rho) + U \geq \xi_1(\rho) + \xi_2(\rho),$$

with

$$(22) \quad \xi_1(\rho) = b_1^2 \int_{\mathbb{R}^3} \rho^{4/3} dx - \alpha \int_{\mathbb{R}^3} W(x) \rho(x) + \alpha \int_{\mathbb{R}^3} \Phi \rho(x) dx,$$

and

$$(23) \quad \xi_2(\rho) = D(\rho, \rho) - \alpha \int_{\mathbb{R}^3} \Phi(x) \rho(x) dx + U$$

Using the Lieb–Yau electrostatic inequality (16) we have

$$(24) \quad \xi_2(\rho) \geq \alpha \frac{z^2}{8} \sum_{j=1}^K \frac{1}{D_j}.$$

On the other hand, it is simple to estimate  $\xi_1(\rho)$  from below, since it is simple to solve the variational principle  $\inf_{\rho} \xi_1(\rho)$ . Thus we get,

$$(25) \quad \xi_1(\rho) \geq -\frac{1}{4} \alpha^4 \left( \frac{3}{4b_1^2} \right)^3 \int_{\mathbb{R}^3} (W - \Phi)_+^4 dx.$$

From (21), (24), and (25) we get

$$(26) \quad \xi(\rho) + U \geq -\frac{1}{4} \alpha^4 \left( \frac{3}{4b_1^2} \right)^3 \int_{\mathbb{R}^3} (W - \Phi)_+^4 dx + \alpha \frac{z^2}{8} \sum_{j=1}^K \frac{1}{D_j}.$$

Now, using (20) we compute,

$$(27) \quad \int_{B_j} (W - \Phi)_+^4 dx = \left( \frac{2ab_2}{D_j} \right)^4 \frac{4}{3} \pi D_j^3 = \frac{64\pi a^4 b_2^4}{3D_j}.$$

Since any Voronoi cell is contained in a half space, one calculates as in [10] that

$$(28) \quad \int_{\Gamma_j \setminus B_j} (W - \Phi)_+^4 dx = \int_{\Gamma_j \setminus B_j} \left( \frac{z}{|x - R_j|} \right)^4 dx \leq \frac{3\pi z^4}{D_j}.$$

Finally, using the estimates (27) and (28) in (26), we get

$$(29) \quad \xi(\rho) + U \geq \frac{\alpha}{8} M \sum_{j=1}^K \frac{1}{D_j},$$

where

$$(30) \quad M = -\frac{1}{4}\alpha^4 \left( \frac{3}{4b_1^2} \right)^3 \left( 3\pi z^4 + \frac{64\pi a^4 b_2^4}{3} \right) + \frac{\alpha z^2}{8}.$$

If  $M > 0$  then  $\xi(\rho) + U > 0$  and the molecule is stable. Using the fact that  $b_2^2 = b^2 - b_1^2$  together with (18) the condition  $M \geq 0$  can be written solely in term of  $b_1$  as

$$(31) \quad a^2 \frac{b^2 - b_1^2}{b_1^6} \leq \left( \frac{4}{3} \right)^2 \frac{1}{2\pi(4\alpha + 9\alpha^5)}.$$

Finally, in order to allow for the largest possible value of  $z$  (equivalently the largest possible value of  $b_2$ ),  $b_1$  must be chosen so that we have equality in (31). Since the left side of (31) is decreasing as a function of  $b_1$  in the allowed interval  $(0, b)$ , we conclude the proof of our Theorem 1.3.

#### Remarks

- i) Note that we do not need a bound on the fine structure constant to ensure stability in this model. This is due to the absence of the exchange term.
- ii) If we set  $\alpha = \frac{1}{137}$  we find stability up to  $z = 71$ , when the parameter  $\lambda = 0.185$ , up to  $z = 74$  when  $\lambda = 0.2$  and  $z = 55$  when  $\lambda = 1/9$ .

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